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(54) HOLLOW TAPE-SHAPED MEMBRANE AND PROCESS FOR PRODUCING SAME

(57) [Summary]

[Object] To provide a hollow membrane that does not necessarily require a binding portion, suppresses sticking of a deposit such as screening residue, and has improved durability for repetitive fouling, etc.

[Solution Means] A hollow tape-shaped membrane having a tape-shaped structure and comprising at least two hollow portion permeation passages continuously extending through in the tape length direction.

[Claims]

[Claim 1] A hollow tape-shaped membrane having a tape-shaped structure and comprising at least two hollow portion permeation passages continuously extending through in the tape length direction.

[Claim 2] The hollow tape-shaped membrane according to Claim 1, characterised in that when the cross-sectional width of the tape-shaped structure is w and the thickness is t, the following expression is satisfied.

$2 \leq w/t \leq 100$

[Claim 3] The hollow tape-shaped membrane according to Claim 1 or 2, characterised in that when the cross-sectional area of the hollow portion of the hollow tape-shaped membrane is S1 and the area of the section surrounded by the outer edge of a cross-section of the tape-shaped membrane is S2, the following expression is satisfied.

$0.1 \leq S1/S2 \leq 6$

[Claim 4] A hollow fibre membrane module comprising the hollow tape membrane according to any one of Claims 1 to 3 and an end-fixing part for fixing an end part of the membrane.

[Claim 5] A process for producing the hollow tape-shaped membrane according to any one of Claims 1 to 3, the process comprising extruding a raw material for a hollow tape-shaped membrane while forming a hollow portion in the membrane cross-section, using a slit-shaped nozzle.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains] The present invention relates to a membrane that is suitable for filtering a highly contaminated liquid, in particular a membrane for a microfiltration membrane or a membrane for ultrafiltration. More specifically, it relates to a hollow tape-shaped membrane in a novel configuration that is used for microfiltration or ultrafiltration and has been improved in terms of entanglement of hollow fibre membranes, which easily occurs when a hollow fibre membrane module is operated, sticking of a deposit on the hollow fibre membrane surface, etc., and to a process for producing same.

[0002]

[Prior Art] Conventionally, a hollow fibre membrane separation method in the field of microfiltration and ultrafiltration has become prevalent in the process water treatment, drinking water treatment, pure water production, food production, pharmaceutical, etc. fields because of energy saving, space saving, power saving, etc. Furthermore, in recent years the method has come into use for high-turbidity water treatment applications such as a second treatment or third treatment in sewage treatment, solid-liquid separation in a water purifier tank, solid-liquid separation of SS (suspended solids) in industrial effluent, direct filtration of river water in a drinking water treatment plant, filtration of industrial tap water, and filtration of swimming pool water. Most hollow fibre membrane modules used in these fields are cylindrical

types, which are used in the conventional microfiltration field and in which hollow fibre membrane is arranged by converging it into a circular shape or a concentric circular shape, or are ones with improved hollow fibre membrane packing ratio or packing configuration.

[0003]

[Problems to be Solved by the Invention] When a filtration treatment of high turbidity raw water is carried out using such a hollow fibre membrane module, hollow fibre membranes easily adhere to each other via a deposit such as organic material or screening residue attached to the hollow fibre membrane surface, and the filtration area of the hollow fibre membrane surface decreases, thus causing a rapid reduction in filtration speed. In order to remove a deposit on the hollow fibre membrane surface, a cake layer or a deposit on the membrane surface is removed by scrubbing with air, backwashing with a permeable liquid, etc., but removal is difficult because of screening residue entangled with the hollow fibre membrane or entanglement between hollow fibres, and there is a problem in terms of ease of restoration by cleaning. As a countermeasure, in the case of a hollow fibre membrane, as described in Japanese Patent No. 2527470, a blind-shaped hollow fibre membrane formed by binding, at fixed intervals along the path of a spinning line, hollow fibre membranes running in parallel has been proposed. Furthermore, JP-A-6-238133 discloses a method for forming a hollow fibre membrane into a blind shape by string knitting, but in a binding portion for combining the hollow fibre membranes, sticking and coalescing is promoted, screening residue becomes entangled more easily, and it is difficult to improve the ease of removing deposits. Moreover, a method of covering a hollow fibre membrane or a tubular membrane with a flat membrane described in JP-A-7-289856 makes it easy to prevent entanglement of hollow fibre membranes or to remove organic material deposited between the hollow fibre membranes, but the filtration area of the hollow fibre membrane module is decreased by covering with the flat membrane, and the production process becomes complicated, which cannot be said to be desirable in practice.

[0004] The object of the present invention is to propose a filtration membrane in a novel configuration that, unlike a conventional hollow fibre membrane module, can prevent hollow fibre membranes sticking to each other due to a deposit such as screening residue, for which removal of a deposit is easy, and that can give good ease of restoration by cleaning. Furthermore, the object is to provide a hollow tape-shaped membrane that can improve mechanical strength without decreasing filtration area, and a process for producing same.

[0005]

[Means for Solving the Problems] In order to accomplish the above-mentioned objects, the present invention has the following constitution. That is, it is "A hollow tape-shaped membrane having a tape-shaped structure and comprising at least two hollow portion permeation passages continuously extending through in the tape length direction.", "The above hollow tape-shaped membrane, characterised in that when the cross-sectional width of the tape-shaped structure is w and the thickness is t, the following expression is satisfied. $2 \leq w/t \leq 100$", "The hollow tape-shaped membrane according to Claim 1 or 2[1], characterised in that when the cross-sectional area of the hollow portion of the hollow tape-shaped membrane is S1 and the area of the section surrounded by the outer edge of a cross-section of the tape-shaped membrane is S2, the following expression is satisfied. $0.1 \leq S1/S2 \leq 6$", "A hollow fibre membrane module comprising any one of the above hollow tape membranes and an end-fixing part for fixing an end part of the membrane.", and "A process for producing the hollow tape-shaped membrane according to any one of the above, the process comprising extruding a raw material for a hollow tape-shaped membrane while forming a hollow portion in the membrane cross-section using a slit-shaped nozzle."

[0006]

[Mode for Carrying Out the Invention] A mode for carrying out the invention is explained below.

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[1] *Translator's note: this wording probably inadvertently left in Japanese original.*

[0007] With regard to the tape used in the present invention, one in which, when the width of the cross-section of the tape-shaped membrane structure is w and the thickness is t, the expression $2 \leq w/t \leq 100$ is satisfied while the average thickness (t) is $0.1 < t < 2.0$ mm and the width (w) is $0.2 \text{ mm} < w < 200$ mm is preferably used. When the cross-section of the tape is not an exact rectangle, the long side of a minimum area bounding rectangle of the cross-section can be defined as the width w, and a single piece[2] as the thickness t.

[0008] With regard to the cross-section forming a permeation passage of the hollow portion of the hollow tape-shaped membrane, when the cross-sectional area of the hollow portion is S1 and the cross-sectional area surrounded by the outer edge of the cross-section of the tape-shaped membrane is S2, the relationship $0.1 \leq S1/S2 \leq 6$ is preferably satisfied.

[0009] The features of the hollow tape-shaped membrane of the present invention are explained by reference to the drawings below; FIG. 1 is a perspective view showing one example of the hollow tape-shaped membrane of the present invention, and the drawings in FIG. 2 are schematic cross-sectional views of hollow tape-shaped membranes.

[0010] The cross-section of the hollow tape-shaped membrane of FIG. 2 (1)[3] has a shape in which circular hollow portion permeation passages 7 are arranged on a straight line at equal intervals. The cross-section of the hollow tape-shaped membrane of FIG. 2 (2) has a shape in which substantially square-shaped hollow portion permeation passages 7 are arranged at equal intervals. The cross-section of the hollow tape-shaped membrane of FIG. 2 (3) has a shape resulting from joining circular hollow fibre membranes at equal intervals. The cross-section of the hollow tape-shaped membrane of FIG. 2 (4) has a shape in which repeating recesses 8 are imparted to the membrane outer edge. The cross-sectional shape of the hollow tape-shaped membrane is not limited to those described above.

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[2] *Translator's note: probably a typographical error in Japanese, should be 'short side'.*

[3] *Figures at end of patent have 2(A), 2(B)... rather than 2(1), 2(2)...*

[0011] As a material for such hollow tape-shaped membranes, a high-molecular-weight polymer normally used for an ultrafiltration membrane or a microfiltration membrane can preferably be used. Examples thereof include cellulose acetate-based, polyamide-based, polyacrylonitrile-based, methacrylate ester-based, polyester-based, polyvinyl alcohol-based, polyolefin-based, polyethylene-based, and polypropylene-based polymers.

[0012] FIG. 3 is a schematic outline of equipment related to the process for producing a hollow tape-shaped membrane of the present invention. There are a pair of opposed drive rollers 15 within a coagulating liquid vessel 14 on a plumb line from a slit-form nozzle 9, and a polymer solution is discharged from the slit-form nozzle 9 into a gas phase and is made to pass through a gap between the opposed drive rollers 15 within the coagulating liquid vessel 14. By so doing, the tape shape can be prevented from twisting in the bath and the ease of following the drafting (stretching) can be improved. The gap between the opposed drive rollers 18[4] may be set freely.

[0013] As a process for producing a hollow tape-shaped membrane, it may be produced by a dry-wet membrane formation method, which is a solution spinning method employing a high-molecular-weight polymer dissolved in a solvent, a wet membrane formation method, or a melt membrane formation method employing a molten high-molecular-weight polymer.

[0014] With regard to a solvent that can be used in solution membrane formation, a known solvent may be used under known conditions. Examples thereof include dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMAC) as solvents for a polyacrylonitrile-based polymer.

[0015] Furthermore, as an injection fluid for forming the hollow portion, a gas or a liquid may be used. With regard to the gas, air, nitrogen, etc. for which discharge pressure and discharge flow rate have been adjusted may be used. With regard to the liquid, a coagulating solution, preferably a coagulating liquid containing a

[4] *Translator's note: assume should be '15'*

common solvent with a polymer solution, is generally used, but it is necessary to allow for coagulation speed changing depending on the conditions.

[0016] FIG. 4 is a schematic diagram of one example of a slit-form nozzle that can be used in the process of the present invention; a high-molecular-weight polymer is discharged from a high-molecular-weight polymer supply hole 21 to a slit part 22, and an injection liquid is discharged to a discharge face 24 from an injection fluid pipe inlet 23 for forming a hollow portion in the membrane cross-section.

[0017] FIG. 5 is a schematic diagram of a discharge face of one example of a hollow portion joining-type slit-form nozzle; a hollow portion joining-type slit-form nozzle 25 has slits 27 arranged in a circular manner so that circular hollow portions are joiningly formed. A hollow portion joining-type slit-form nozzle 26 has slits 27 arranged in a rectangular manner so that rectangular hollow portions are joiningly formed. The shape and arrangement of the slits are of course not limited to those illustrated.

[0018] Specifically, in the case of solution membrane formation spinning, a raw material solution is discharged from a slit part using a slit-form nozzle as shown in FIG. 4 and a precision metering gear pump, another aqueous solution is discharged to a temperature and humidity regulated dry part from injection liquid holes arranged in the middle, this is followed by discharge into a coagulating liquid containing an aqueous solution, and a membrane thus made into a tape is pulled out from the coagulating liquid vessel. Subsequently, after repeating a solvent removal operation in washing vessels, a thermal treatment, a membrane surface treatment, etc. and then winding-up are carried out, and cutting into the required module length is carried out. A polymer solution for membrane formation spinning preferably has a viscosity range of 0.1 to 3000 poise, more preferably 10 to 2000 poise, and yet more preferably 30 to 1500 poise, and a dry length is in the range of 1 to 200 mm, preferably 1.5 to 100 mm, and yet more preferably 2 to 50 mm. Solvent diffusion in the polymer solution depends greatly on coagulation bath liquid temperature, and the coagulation bath liquid temperature is in the range of -30°C to 95°C, preferably -5°C to 65°C, and yet more preferably 15°C to 45°C. The membrane formation spinning

drafting (stretching) ratio is determined by the discharge line speed in the slit-form nozzle and the take-up speed of the rollers in the bath, and the drafting ratio is in the range of 0.1 to 30, and preferably 0.5 to 20.

[0019] In the case of molten membrane formation spinning, for example, molten polyethylene is extruded via the slit part of a joining-type slit-form nozzle of FIG. 4[5], adjacent molten polyethylene fuses and joins to thus form a hollow portion, following this cooling/solidifying and cold drawing are carried out so that a lamellar layered structure is taken, and hot drawing is carried out so as to give a uniform hole diameter by plastic deformation.

[0020] FIG. 6 shows schematic front and split cross-section diagrams of a hollow tape-shaped membrane module related to the present invention. One end part of a hollow tape-shaped membrane 1 is embedded in a casting resin, and the other end part is fixed by a casting resin as a water-collecting part side 28. Raw water is made to flow from a supply hole 29, and permeated water may be taken out from an outlet 30 and used.

[0021] As a water-collecting member, a general-purpose thermoplastic resin such as vinyl chloride, polycarbonate, polysulfone, polyethylene, polystyrene, polypropylene, or polymethyl methacrylate, or a metal such as stainless steel may be used.

[0022] Furthermore, as main casting resins, reactive resins such as epoxy, polyurethane, polyester, phenol, and polyacrylate may be used.

[0023] The dimensions of the module equipped with the tape-shaped hollow portion-forming membrane are not uniquely defined since membrane module design, maintenance of a unit device incorporating a membrane module, etc. have to be taken into consideration, but it is possible to increase the dimensions by connecting membrane module units.

[0024] As hereinbefore described, features of the hollow tape-shaped membrane of the present invention are summarised as follows.

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[5] *Translator's note: the joining-type slit-form nozzle was earlier described with reference to FIG. 5*

[0025] Unlike a conventional hollow fibre membrane, a binding portion is not required, there is hardly any entanglement between membranes due to them converging, and sticking of a deposit such as screening residue is therefore not easily promoted. Furthermore, any deposit once stuck can be easily cleaned by physical cleaning such as air scrubbing, thus giving good ease of restoration. Moreover, when the hollow tape-shaped membrane of the present invention is made into a module, entanglement between membranes and sticking of a deposit such as screening residue are suppressed without binding the hollow fibre membranes or degrading the packing density, and good ease of restoration by cleaning and a stable permeation flux can be obtained. Furthermore, compared with a hollow fibre membrane, the mechanical strength improves and the operational time of the membrane module can be extended. Moreover, the hollow tape-shaped membrane may be produced by adding a slit-form nozzle to a conventional solution membrane formation spinning technique or molten membrane formation spinning technique.

[0026]

[Examples]

Example 1

Membrane formation spinning was carried out by a dry-wet method using a production system of FIG. 3. That is, a polyacrylonitrile-based polymer (molecular weight: about 250,000) was dissolved in dimethyl sulfoxide (DMSO) solvent at a solution concentration of 12.5 wt percent. An injection fluid employed an 80 wt percent aqueous solution of dimethyl sulfoxide (DMSO).

[0027] The polymer solution described above was supplied using a precision metering gear pump via a slit part of a slit-form nozzle 9 (slit width: 1.1 mm, slit length: 12 mm, outer diameter of capillary 0.6 mm, inner diameter 0.3 mm, capillary gap: 0.9 mm) incorporated into a membrane formation spinning head 12, and the injection liquid was supplied to 12 capillary holes using a precision metering gear pump. After discharging at a dry length of 20 mm within a dry part atmosphere control hood adjusted so as to have an absolute humidity of substantially 0.0272 kg

(water)/kg (dry air), discharge into a coagulating liquid of 15 wt percent dimethyl sulfoxide at a temperature of 30°C was carried out, and the hollow tape-shaped membrane was pulled out from a take-off roller 16 via in-bath opposed rollers 15 in a coagulating liquid vessel 14, and wound up by a winder after a solvent removal vessel 18, etc. When the cross-sectional dimensions of the hollow tape-shaped membrane after membrane formation spinning were measured, the results were that the average tape width (w) was 11.2 mm, the average thickness (t) was 826 μm, the average hole size of hollow portion-forming holes was 440 μm, and the aspect ratio (L/S) was 0.95.

[0028] Example 2, Comparative Example 1

A single-ended water-collecting type module employing the hollow tape-shaped membrane 1 according to the present invention was prepared as shown in FIG. 6 using the tape-shaped membrane shown in Example 1 (Example 2). Furthermore, a single-ended water-collecting type module was prepared using, instead of the tape-shaped membrane, a bundle of hollow fibre membranes having the same membrane surface area (Comparative Example 1). Compared with Comparative Example 1, Example 2 showed about 2.3 times the elapsed time until operating pressure difference decreased to a predetermined level. Furthermore, Comparative Example 1 showed a large number of fibre cuts in the hollow fibre membrane module caused by air scrubbing, whereas Example 2 showed no tape cuts in the hollow tape-shaped membrane.

[0029]

[Effects of the Invention] The hollow tape-shaped membrane and the process for producing same related to the present invention have the constitutions described above. Since, unlike a conventional hollow fibre membrane, the hollow tape-shaped membrane thus produced does not necessarily require a binding portion, and there is hardly any entanglement between membranes due to them converging, sticking of a deposit such as screening residue can be greatly reduced. Furthermore, unlike a hollow fibre membrane, filtration area can be guaranteed without degrading the

packing ratio, and since the mechanical strength improves, the durability for repetitive fouling, etc. can be improved. Moreover, with regard to the constitution of a module, the same constitution as that of a hollow fibre membrane module can be employed, and the above-mentioned effects can be exhibited.

[Brief Description of Drawings]

[FIG. 1] A perspective view showing one example of the hollow tape-shaped membrane of the present invention.

[FIG. 2] Cross-sectional views showing examples of the hollow tape-shaped membrane of the present invention.

[FIG. 3] A schematic diagram of production equipment used in the production process of the present invention.

[FIG. 4] Views of a slit-form nozzle used in the production process of the present invention. (A) front view. (B) bottom view. (C) cross-section along A-A' in (A).

[FIG. 5] Schematic drawings of joining-type slit-form nozzles used in the production process of the present invention.

[FIG. 6] A transparent view of a module employing the hollow tape-shaped membrane (A) and a cross-sectional view along A-A' (B).

[Explanation of Reference Numerals and Symbols]

1: Hollow tape-shaped membrane

2: Hollow tape-shaped membrane in which circular permeation passages are linearly arranged

3: Hollow tape-shaped membrane in which rectangular permeation passages are linearly arranged

4: Hollow tape membrane in which circular hollow fibre membranes are joined to each other

5: Hollow tape-shaped membrane in which circular permeation passages are formed and a regular concavoconvex shape is imparted to the membrane outer edge

6: Cross-section of hollow tape-shaped membrane

7: Permeation passage

8: Regular concavoconvex shape on membrane outer edge

9: Slit-form nozzle

10: Injection liquid metering pump

11: Polymer metering pump

12: Membrane formation spinning pack

13: Hood

14: Coagulating liquid vessel

15: Opposed rollers

16: Take-off roller

17: Hollow tape-shaped membrane

18: Solvent removal vessel

19: Membrane surface treatment vessel

20: Winder

21: Polymer supply hole

22: Polymer discharge slit

23: Injection fluid pipe

24: Injection fluid discharge hole

25: Joining-type slit nozzle (circular hollow portion type)

26: Joining-type slit nozzle (rectangular hollow portion type)

27: Slit shape

28: Water-collecting part

29: Raw water supply hole

30: Permeated water outlet

31: Upper part fixing end

32: Lower part fixing end